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GB 2169496 A GB 2118028 A EP 0642846 A1
WO 83/01400 A1 US 4898650 A

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(54) Process for cleaning or decontaminating an object by means of an ultraviolet laser beam together with apparatus for implementing the process

(57) A process for cleaning or decontaminating the surface of an object such as vessel (20) by using an ultraviolet laser beam (22). The ultraviolet laser beam is used under conditions selected so that, depending on the material used to produce the object, it causes surface stripping of the object, said stripping including superficial removal of the material of which the object itself is composed. For stainless steel a reducing gas, particularly an inert fluorinated gas, is used.

The beam 22 is directed through guide 23. Inert gas, such as argon, and possibly reducing gas supplied from a controller. End piece 55 of arm 23 rotates freely with respect 40 portion 45, and is driven from motor 54 via toothed wheel 56.

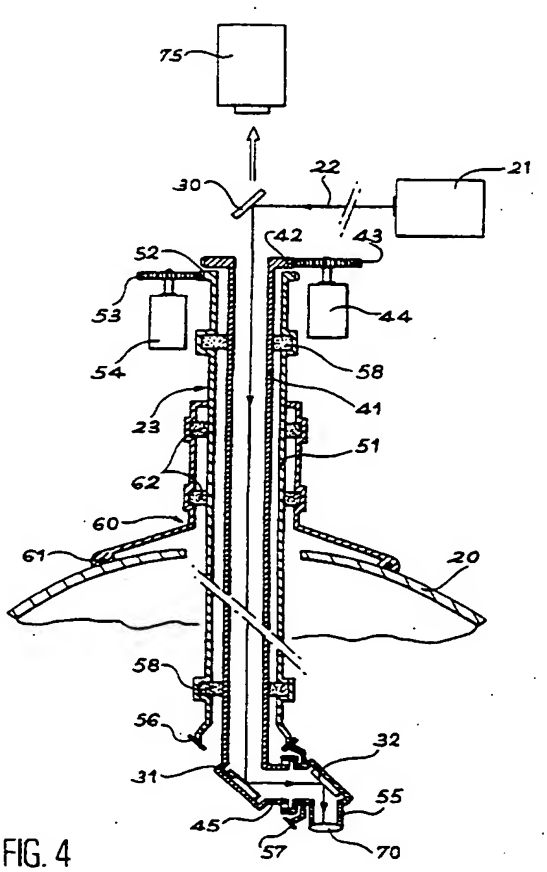

FIG. 4

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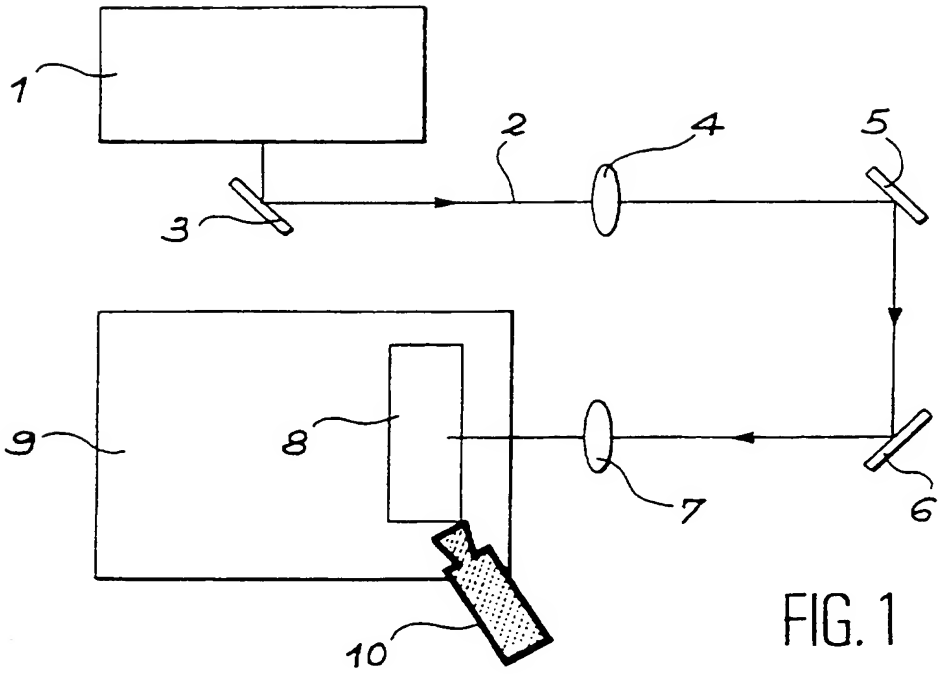
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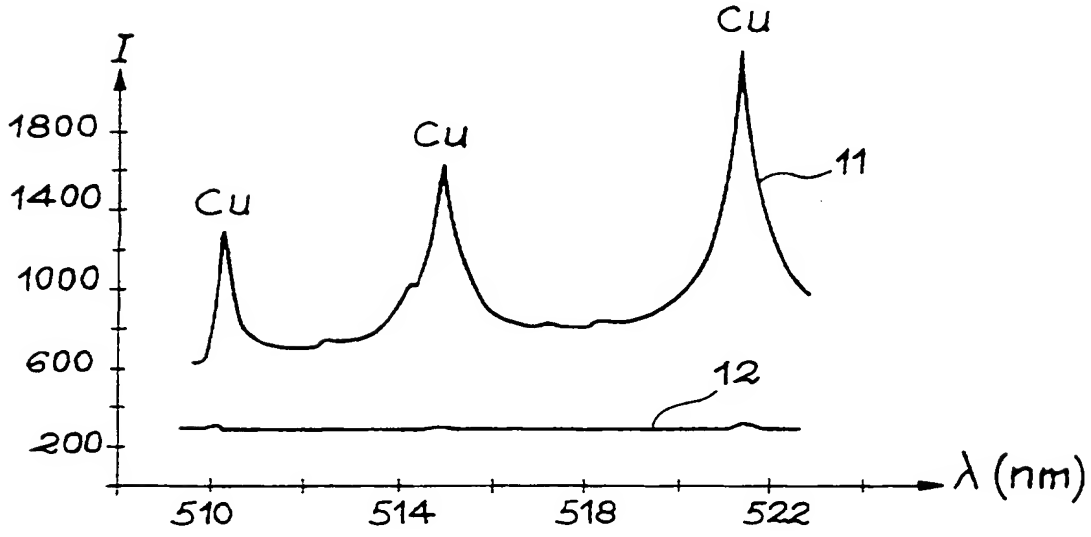
FIG. 1


I
1800
1400
1000
600
200
Cu
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11
12
510
514
518
522
λ (nm)

FIG. 2

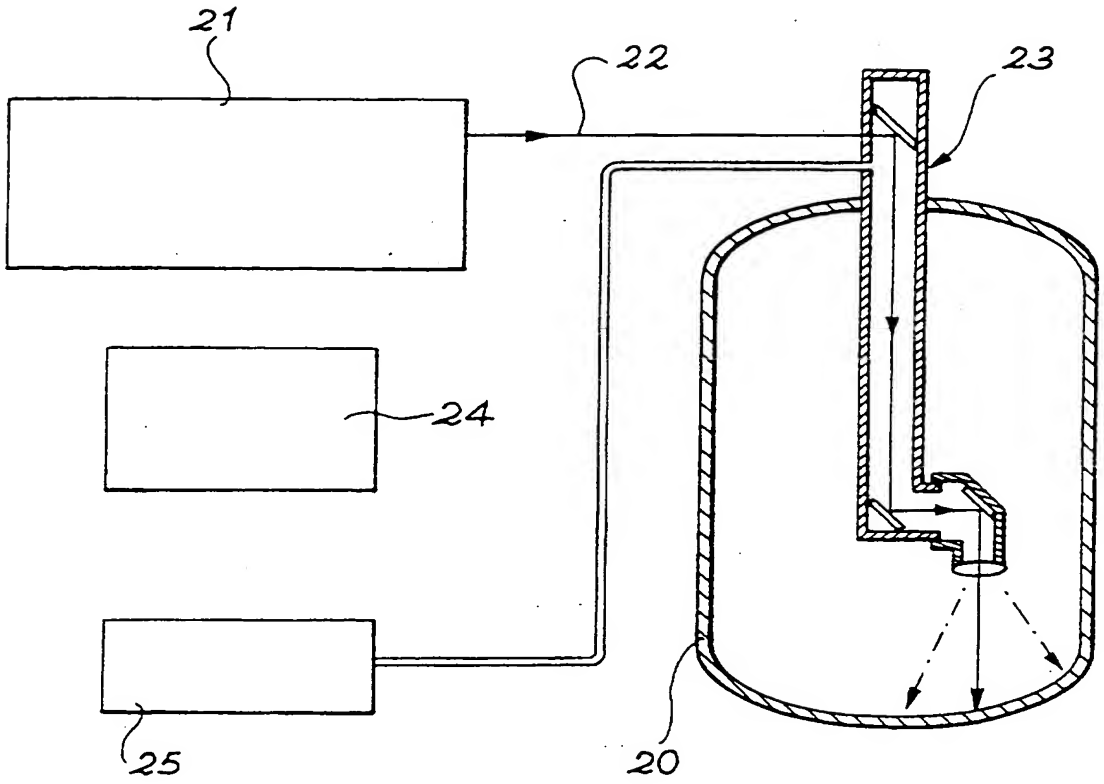

FIG. 3

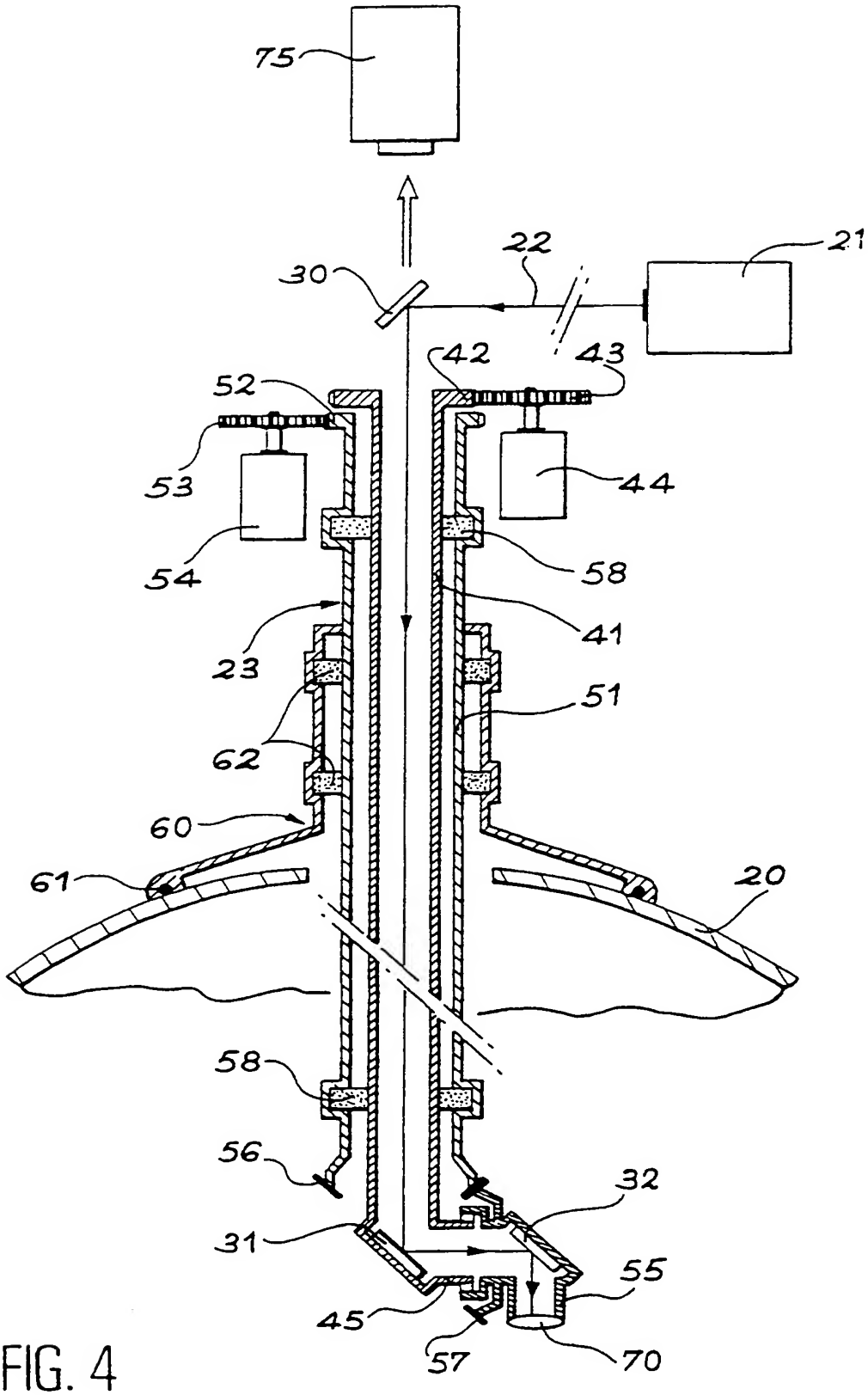
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FIG. 4

2316528

PROCESS FOR CLEANING OR DECONTAMINATING AN OBJECT BY MEANS OF AN ULTRAVIOLET LASER BEAM TOGETHER WITH APPARATUS FOR IMPLEMENTING THE PROCESS

DESCRIPTION

The present invention relates to a process for cleaning or decontaminating the surface of an object by using an ultraviolet laser beam. It also relates to an apparatus for implementing said process.

The use of laser beams to clean and decontaminate the surface of an object has been described in many publications. The following documents may be cited from among these publications:

WO 90/07988 discloses the use of a laser beam to clean a surface, the laser beam being manually guided during the cleaning operation. The power of the laser beam is of the order of several tens of MW/cm^2 at a wavelength of the order of a micron. The technique disclosed by this document has drawbacks related to repetitiveness, lack of accuracy, onerousness and inefficiency on certain materials.

FR-A-2 525 380 describes a decontamination process that uses a beam of light emitted by a YAG laser at a wavelength of 1.06 μm. This process was developed to remove the thin film of oxide from the surface of metal objects that have been contaminated by radioactive elements. The process cannot, however, be used to treat the substrate of the oxide layer, i.e. the purely metallic section of the object. Moreover, the effect of the laser beam is essentially thermal and this makes it unsuitable for decontaminating plastic objects. In fact, the laser beam causes superficial melting of a plastic object, which has the effect of definitively

coating the contaminants in the plastic material. This has the opposite effect to that required.

In FR-A-2 700 882 the decontamination of a surface contaminated by radioactive elements is conditional on the maintenance of a liquid on the surface to be treated. The use of this liquid has a number of drawbacks, for example removal of the liquid after termination of the process.

FR-A-2 707 877 suggests using an ultraviolet laser beam and a reactive gas such as oxygen. Experiments have shown that the presence of oxygen during decontamination operations leads to immediate reforming of oxide layers on the treated metals. These layers again trap the contaminants, which is contrary to the desired result. This document also refers to a trapping zone for particles dislodged from the treated surface and then emitted. This trapping zone is located between 2 and 10 mm from the treated surface. This short distance is a drawback for implementation of the procedure.

WO 95/13618 describes a process that uses a laser beam to locally melt the surface of a metal object to be treated, decontamination occurring through elimination of the melted metal. A drawback of this method is the need to work in contact with the surface to be decontaminated. Furthermore, melting the metal is a major drawback because it damages the state of the surface, creates slag and again traps neighboring contaminants.

The processes described above using the prior art thus have a certain number of drawbacks.

They normally use laser beams at wavelengths in the infra-red or visible sectors of the spectrum. They consequently produce superficial melting of metallic materials, which gives rise to serious drawbacks.

When such techniques are manually implemented scanning of the surface to be treated is incomplete. This results in either leaving tiny areas untreated or make it necessary to perform repeat treatment phases. Where the decontamination concerned is nuclear, another major drawback is the risk of staff being irradiated by ionizing radiation.

One of the procedures described concerns the use of a laser beam combined with sprinkling of a liquid supposed to have reinforcing properties. Although water-based, the liquid in question is difficult to apply, eliminate and treat. Moreover, research carried out by the inventors of the present invention has shown that microcracks form under each residual drop of liquid. These microcracks produce a porous surface that is very subject to recontamination.

The plasma heat produced by the impact of the laser beam or the surface stripping caused by laser shock in combination with use of a reactive gas such as oxygen causes immediate very pronounced reoxidation of the surface. Such reoxidation is capable of causing recontamination.

The present invention has been designed to overcome all the drawbacks of the prior art. The inventors carried out a certain number of investigation that unexpectedly gave rise to a process for the remote decontamination or cleaning of plastic or metal surfaces. This process can easily be automated and, depending on the circumstances, may include addition of a gas that is beneficial for the final state of the surface to be treated, e.g. for polishing the surface without causing reoxidation.

The invention therefore relates to a process for cleaning or decontaminating the surface of a metallic object that uses the impact of an ultraviolet laser beam, characterized in that the ultraviolet laser beam

is used under conditions selected so that, depending on the material used to produce the object, it causes surface stripping of the object, said stripping including superficial removal of the material of which the object itself is composed.

If an oxide layer has developed on the surface of said metal object, said operating conditions are those that produce vaporization of the oxide and creation of a plasma that causes superficial removal of the material of which the object itself is composed.

Depending on circumstances it may be advantageous for the operating conditions to include impacting of the laser beam on the said object to occur in an atmosphere of gas that is inert to the material composing the object, e.g. an argon atmosphere.

It may also be advantageous for the laser beam to impact on said object under reducing conditions. These reducing conditions may be obtained by the presence of at least one suitable additive to the inert gas atmosphere.

The invention also relates to an apparatus for cleaning or decontaminating the internal surface of a recipient by using the impact of an ultraviolet laser beam, characterized in that it comprises a laser emitting said ultraviolet laser beam under conditions selected so that, depending on the material constituting the object, it causes stripping of the object, said stripping including superficial removal of the material of which the object itself is composed, means for transmitting the laser beam to said internal surface and comprising mirrors to direct the laser beam at an area of the internal surface of the recipient, said mirrors being disposed such that, under the influence of a control device, the entire surface to be cleaned or decontaminated is scanned, the apparatus

also comprising means for removing materials resulting from the stripping of said internal surface.

Other characteristics and advantages of the present invention will be better understood from the following description. The description is non-limitative and refers to the attached Figures where:

- Figure 1 is a schematic diagram of the experimental set-up used to design the invention,
- Figure 2 shows the emission spectrum of the plasma produced by a laser beam on an oxidized copper surface,
- Figure 3 shows an apparatus using the principle of the invention for decontaminating a container,
- Figure 4 is a detailed view of the apparatus shown in Figure 3.

The invention uses an ultraviolet laser beam, i.e. at a wavelength of between 10 and 400 nm.

The experimental set-up shown in Figure 1 uses an XeCl laser, numbered 1 in the Figure, emitting a beam of light at a wavelength of 308 nm in 28 ns pulses. The type of laser used is one of the most powerful currently available, i.e. a 250 HZ LambdaPhysik 400 mJ.

The set-up in Figure 1 uses straightforward image transfer techniques to direct the laser beam. Laser beam 2 is first reflected by mirror 3 before passing through a first focusing lens 4; it is then reflected by mirrors 5 and 6 successively before passing through the second focusing lens 7 (focal length 0.5 m) to reach target 8 disposed inside protective container 9. A video camera 10 is used to monitor the impact of laser beam 2 on target 8.

Using this set-up the power of the laser beam measured on the target is 300 mJ per pulse. Mirrors 5 and 6 can be rotated to direct laser beam 2 over the entire surface of the target.

Treatment of three different materials using the process according to the invention will now be described. Using these examples, those skilled in the art wishing to apply the invention to other materials will only need to carry out tests using the techniques available without having to show particular inventiveness. These tests will give them information for any given material on the laser beam power ratings required at the surface of the target and the optimal conditions required for implementing the invention.

Example I

The first example concerns treatment of a plastic coating, in this example an epoxy paint.

The power of a single ultraviolet photon is enough directly to excite the electronic levels close to or greater than the dissociation limit of the organic bonds. The process is photochemical with weak thermal effects.

At 0.5 J/cm² the coating is not stripped; this value is thus the stripping threshold. Stripping becomes effective at 0.7 J/cm², maximum efficiency being attained at 1.8 J/cm². At a repeat firing rate of 250 Hz, a stripping rate of 0.5 m²/h can be achieved for a depth of 30 μm. It should also be noted that variations of up to 45° in the angle of incidence of the laser beam have very little effect on stripping efficiency.

For plastic materials the maximum power rating of the laser beam is that above which the plastic starts melting or burning.

Example II

In the second example the target is a copper mass with a naturally-oxidized surface.

A sufficiently powerful laser beam (2 J/cm²) vaporizes the copper oxide layer and a plasma forms because this oxide layer is highly absorbent of ultraviolet radiation. Analysis of plasma light emissions can be used to determine the elements composing the material on which it has formed.

Curve 11 of the graph in Figure 2 shows the emission spectrum of the first two laser firings. The three peaks of the curb at 510.55 nm, 515.32 nm and 521.82 nm do in fact correspond to the emission of copper atoms from the stripped area.

Starting from the third laser firing, the emission spectrum (curve 12 on the graph of Figure 2) shows that no more copper is emitted since plasma is no longer formed, the coefficient of absorption of the metal being low. A considerably higher laser flux is required for plasma to recur.

The process according to the invention is therefore very efficient and highly selective since only two pulses are required to strip the mass of oxidized copper down to the substrate.

It has been noted that an acoustic signal is emitted during the formation of plasma. An acoustic signal may therefore be recorded during the interaction between the laser beam and the oxidized surface for the first two firings. The third laser firing produces a very low acoustic signal.

Example III

In the third example the target is a mass of Fe/Cr/Ni stainless steel composed of 72% iron, 18% chrome and 10% nickel by weight. Aging has caused an oxide layer several tens of microns thick to form on the steel. It has been found that in order to

decontaminate this type of target it is essential first to break down the oxide layer formed during aging.

A 2 J/cm² flux easily vaporizes the oxide layer while emitting an approximately 8 mm long highly-luminous plasma. The sudden expansion of the plasma simultaneously produces an acoustic bang.

A few firings are enough to totally eliminate the oxide layer, showing the process to be highly efficient from this point of view. The subsequent firings at 3 J/cm² on the stripped, shiny metal substrate do not give rise to production of any plasma or acoustic bang. However, decontamination as part of the decommissioning of nuclear installations imposes high decontamination factors that cannot be achieved without removing material from the metal substrate itself. At the same time, care must be taken not to melt the metal superficially and reoxidize the treated surface since both processes trap contaminant elements. This argument leads to an exact definition of the good operating conditions required by stainless steels.

If, in fact, laser irradiation of the surface of the steel mass is continued in an air atmosphere once the oxide layer has been removed, it will be found that short periods of irradiation cause blackening of the treated surface and that longer irradiation not only increases blackening but causes the appearance of a brick oxide structure due to the differences in thermal stress between the metal and its oxide. This new oxide layer is undesirable because it absorbs laser photons and has a screening effect following stripping; it also tends to trap contaminating particles and to reduce the decontamination factor thereby causing deterioration in the state of the surface.

The inventors carried out a series of experiments to overcome these phenomena. The experiments used a number of samples of this steel and an analysis of the

surfaces was carried out using XPS photoelectron spectroscopy and ionic bombardment. This analysis method causes abrasion of samples at a rate of several nm/min (2 nm/min in the present experiments), making it possible to identify the deeper physico-chemical structures of the treated samples.

Several samples were examined using these techniques, starting with an untreated sample (i.e. one retaining its initial oxide layer) followed by samples treated under a variety of conditions.

An untreated sample is composed as follows: to a depth of 0.13μm the iron and chrome are mainly present as oxides while the nickel is in its metallic state. The composition of the sample remains constant beyond a depth of 0.13μm, iron oxide being present. At a depth of 0.48μm the relative concentrations of Fe, Cr and Ni measured are 70.9%, 21.9% and 7.2% respectively by weight. Given the measurement accuracy of the technique used, these values are a good match with the certified composition of the sample, i.e. 72%, 18% and 10% by weight.

A sample treated in air as described above is composed as follows: to a depth of 1.1μm, apart from a small quantity of metallic nickel the sample consists almost entirely of oxygen and metal oxides. At a depth of 1.3μm the ratio of iron oxide to metallic iron is still approximately 50%. There has therefore been reforming of oxide and oxygen present.

To a depth of 0.4μm the composition of a sample treated in argon is more or less correct, i.e. 70% iron, 20% chrome and 11% nickel by weight. Between the surface of the sample and this depth, the oxygen remains present even though less concentrated than for irradiation in air.

A sample treated in argon in the presence of alcohol presents a very clean surface because a correct

elementary composition is obtained after a few minutes' analysis and because the oxygen concentration is very low.

It is therefore highly advantageous for stripping according to the invention to be carried out in an inert gas of which argon is the most convenient. Nitrogen should be avoided because it can cause nitriding. Since under current decontamination conditions it is difficult to exclude oxygen totally, it is preferable to work in reducing conditions achieved through the use of additives. For example, a jet of pure argon can be replaced with argon containing tiny quantities of hydrogen (less than 4% by volume) or hydrocarbon compounds such as ethanol, sugars with low molecular weights or polyalcohols. Under these circumstances risk of recarburation of the surface is attenuated by the presence of carbon monoxide produced in situ, for example:

$$CH3-CH2-OH \rightarrow CO+CH4+H2.$$

The use of such additives can produce fine polished surfaces after irradiation with a laser beam. The rare aerosols trapped on small, highly-effective filters vary in color from light brown to a very deep black.

Interesting results have also been obtained by using fluoridated additives, e.g. sulfur hexafluoride or freons than present no danger for the operator. By displacing oxygen by a more powerful oxidant such as fluorine, volatile metallic compounds may also form within the plasma. Stripping kinetics have been found to be more rapid in the presence of SF6.

These favorable conditions should be applicable to a large number of potential contaminants, e.g. the actinides.

Decontamination apparatus

Figure 3 shows a decontamination apparatus. Reference 20 is a leaktight vessel to be decontaminated; this vessel may be any type of boiler, steam-generating unit with tubular plate, etc.

The apparatus comprises a 250 HZ LambdaPhysik Exciplex (XeCl) 400 mJ laser 21. Laser 21 sends a light beam 22 to vertical laser-beam guide arm 23 used to direct the beam onto the internal surface of the vessel to be decontaminated. The apparatus further comprises a unit 24 for controlling the movement of the laser beam and a gas control wagon 25.

Figure 4 shows details of guide arm 23. This arm has to operate in highly-contaminated areas and must be reliable, i.e. simple and robust. This is why it was decided to use only two axes of rotation to scan the entire inner surface of the vessel (4 π sr).

Laser beam 22 arrives horizontally at the top of the apparatus where semi-transparent mirror 30 sends it vertically inside guide arm 23 to directing mirrors 31 and 32. Mirrors 31 and 32 may be rotated respectively by two coaxial tubes 41 and 51.

Internal tube 41 comprises a vertical section whose upper end is outside vessel 20. The rim of this end is a toothed wheel that cooperates with a toothed wheel 43 driven by a motor 44 to produce a gear system. The lower end of the vertical section of the tube lies within vessel 20 and bears mirror 31 that is inclined at 45° from the vertical. The lower end of the tube is extended horizontally by small section 45. This small section 45 bears a small 90° elbow tube 55 that rotates freely with respect to section 45. Small tube 55 bears mirror 32 that is inclined at 45° from the vertical and disposed facing mirror 31.

The rim of the upper end of external tube 51 is a toothed wheel 52 that coordinates with a toothed wheel 53 driven by a motor 54 to produce a gear system. The lower end of tube 51 also has an edge that is a toothed wheel 56 that coordinates with toothed wheel 57 that is integral with tube 55.

Motors 44 and 54 are thus disposed outside vessel 20. Guide arm 23 rests on the dome of vessel 20 which has previously been pierced by means of apparatus 60. Apparatus 60 is fitted with an O-ring 61 that provides a leaktight seal with the dome of vessel 20. A gland 62 is also provided to allow free rotation of external tube 51. Glands 58 disposed between tubes 41 and 51 ensure that said tubes rotate freely of one another.

Laser beam 22 emitted by laser 21 is reflected by semi-transparent mirror 30 inside guide arm 23 in the direction of mirror 31 that reflects it towards mirror 32 where the beam is again reflected to be directed towards focusing lens 70.

Because plasma emission is noisy, it is advantageous to dispose a microphone on the dome of the vessel in order to monitor removal of the oxide layers.

Since mirror 30 is semi-transparent a video camera 75 is placed above guide arm 23 to observe along the same optical trajectory the impact of the laser beam on the walls of the vessel. The light from the plasma emitted near the treated surface is also sent along the same optical trajectory for spectro-photometric analysis. It can therefore be determined what ions have been removed from the surface and are present in the plasma.

Control unit 24 (see Figure 3) includes the control modules of the stepping motors, the various power supply units and the connectors. Exchanges between the control modules and a micro-computer that manages the implementation of the process may be via an

RS 232 C serial link. Dialogue between the modules occurs using a pre-established digital communications protocol that is not subject to electromagnetic disturbance. Scanning by the laser beam of the surface to be treated may be coupled to a three-dimensional image that is pre-programmed into the control computer of the apparatus.

The gas control wagon 25 comprises bottles of the gas to be injected, for example argon, and an additive such as those described above. The gas is directed into the laser impact area by means of a nozzle. It also comprises two metering pumps of which one recycles ambient gases after fine filtration through an electrofilter and a high-performance filter. Recycled gas is also used to blow-clean lens 70. The second pump keeps the vessel 20 under negative pressure using techniques known in the field of nuclear decontamination.

This apparatus can be used to implement the process according to the invention automatically and therefore without inconvenience to operating staff. It also monitors and filters ambient gases.

CLAIMS (GB, JP)

1. Process for cleaning or decontaminating the surface of a metallic object (8, 20) using the impact of an ultraviolet laser beam (2, 22) characterized in that the ultraviolet laser beam is used under conditions selected so that, depending on the material constituting the object, it causes stripping of the object, said stripping including superficial removal of the material of which the object itself is composed.

2. Process according to Claim 1 characterized in that, an oxide layer being formed on the surface of said metallic object, said operating conditions are such as to cause vaporization of the oxide and the creation of a plasma that causes superficial removal of material of which the object itself is composed.

3. Application of the process according to Claim 2 for cleaning or decontaminating a copper object characterized in that the power of the laser beam is of the order of 2 J/cm^2.

4. Process according to Claim 2, characterized in that among the said operating conditions is included the fact that the impact of the laser beam on said object occurs in an atmosphere of a gas that is inert for the material of which the object is composed.

5. Process according to Claim 4 characterized in that the inert gas is argon.

6. Process according to Claim 4 or 5 characterized in that among the said operating conditions is included the fact that the impact of the laser beam on said object occurs under reducing conditions or addition of a gas composed of hydrogen or hydrocarbon compounds.

7. Process according to Claim 6 characterized in that the reducing conditions are obtained by the

presence of at least one appropriate additive in the inert gas atmosphere.

8. Process according to Claim 7 characterized in that the said additive is a fluoridated compound that, under the effect of a laser beam, volatizes metal atoms and gives greater erosion of the metal.

9. Application of the process according to any of Claims 6 to 8 to the cleaning or decontamination of a stainless steel object, characterized in that the power of the laser beam is of the order of 2 J/cm^2 or more.

10. Apparatus for cleaning or decontaminating the internal surface of a container (20) by using the impact of an ultraviolet laser beam, characterized in that it comprises a laser (21) emitting said ultraviolet laser beam (22) under conditions selected so that, depending on the material constituting the object, it causes stripping of the object, said stripping including superficial removal of the material of which the object itself is composed, means for transmitting the laser beam to said internal surface and comprising mirrors (30, 31, 32) to direct the laser beam (22) at an area of the internal surface of the recipient (20), the mirrors (30, 31, 32) being disposed such that, under the influence of a control device, the entire surface to be cleaned or decontaminated is scanned, the apparatus also comprising means for removing materials resulting from the stripping of said internal surface.

11. Apparatus according to Claim 10 characterized in that the means of conveying the laser beam to said internal surface consist of two mirrors (31, 32) and two coaxial tubes (41, 51) that penetrate the recipient and can rotate upon themselves, each coaxial tube (41, 51) moving one of said mirrors (31, 32).

12. Apparatus of Claim 10 or 11 characterized in that is also comprises means for injecting an inert gas

at the internal surface of the recipient being subjected to the impact of the laser beam (22).

13. Apparatus according to any of Claims 10 to 12 characterized in that it also comprises means for injecting a reducing additive at the internal surface of the recipient being subjected to the impact of the laser beam (22).

14. Apparatus according to any of Claims 10 to 13 characterized in that it also comprises means for transmitting an image of the cleaned or decontaminated surface to an observation camera (75).

15. Apparatus according to any of Claims 10 to 14 characterized in that when the impact of the laser beam (22) on said internal surface (20) causes formation of plasma, means are provided to transmit the light from the plasma to a spectrophotometric analysis apparatus.

16. Apparatus according to any of Claims 10 to 15 characterized in that when the impact of the laser beam (22) on said internal surface (20) causes formation of plasma, a sound sensor is provided to signal the formation of the plasma.

The Patent Office

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Application No: GB 9716447.9
Claims searched: 1 to 16

Examiner: Michael Conlon
Date of search: 28 November 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): A4F (FQX), G6R (R7)

Int Cl (Ed.6): B08B, G21F

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB2169496 A	(STC) whole document	1 and 10 at least
X	GB2118028 A	(Maxwell) the Example	1 and 10 at least
X, Y	EP0642846 A1	(Onet) page 1 lines 6 to 12	1 and 10 at least
Y	WO83 01400 A1	(First of Chelsea) Figure 1	10 at least
X	US4898650	(AMP) whole document	1 and 10 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.